

# The isotopic effects of electron transfer: an explanation for Fe isotope fractionation in nature

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We present both a newly-developed theory and preliminary experimental results that delineate the relationship between driving force in a charge transfer reaction and resulting Fe isotope fractionation. The theory, based on Marcus's chemical kinetics theory for electron transfer (*Ann. Rev. Phys. Chem* **15**1964, 155), predicts that fractionation increases linearly with driving force with a proportionality related to two factors: the difference between isotopic equilibrium exchange, and the reorganization energy along the reaction coordinate. The theoretical predictions were confirmed by measurements of isotopic fractionation associated with electroplating iron metal from a ferrous chloride solution. Isotope fractionation of electroplated Fe was measured as a function of applied electrochemical potential. As plating voltage was varied from  $-50$  mV to  $-2.0$  mV, the  $\delta^{56}\text{Fe}$  increased from  $-0.106(\pm 0.01)$  to  $-2.290(\pm 0.006)$  ‰, with corresponding  $\delta^{57}\text{Fe}$  values of  $-0.145(\pm 0.011)$  to  $-3.354(\pm 0.019)$  ‰. The slope of the line created by plotting  $\delta^{56}\text{Fe}$  vs

$\delta^{57}\text{Fe}$  is equal to  $0.6723(\pm 0.0032)$ , consistent with fractionation due to a kinetic process involving unsolvated iron atoms. This study demonstrates that there is a voltage-dependent isotope fractionation associated with the reduction of iron. The magnitude of fractionation is similar to observations of Fe reduction by certain bacteria, suggesting that electrochemical processes may be responsible for observed biogeochemical signatures. Charge transfer is a fundamental physicochemical process involving Fe as well as other transition metals with multiple isotopes. Partitioning of isotopes among elements with varying redox states holds promise as a tool in a wide range of the Earth and environmental sciences, biology, and industry.